Theory of phase transitions in semiconductors of the A_4B_6 group

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An electron spectrum model with band overlapping in the vicinity of Brillouin-zone L points in the cubic phase is proposed for semiconductors of the A_4B_6 group with band inversion. Allowance for interband transitions and Coulomb and electron-phonon interaction leads to a first-order phase transition to the semiconductor state. Bose condensation of optical phonons occurs in this case and it leads to a displacement of the sublattices; interaction between the electrons and the acoustic modes, on the other hand, leads to rhombohedral distortion of the high-temperature cubic structure. The order parameter, the phase of which determines the direction of the sublattice displacement is rigidly related to the phase of the interband-transition matrix element. In accordance with the model, a correlation between the structural and superconducting transition temperatures is observed for the given class of doped semiconductors and their alloys.

1. INTRODUCTION

Keldysh and one of the authors[1] have considered the possibility of a phase transition into the dielectric state as a result of electron-hole pairing in the model of a semimetal with isotropic strongly-overlapping bands, the extrema of which are located at one point of the Brillouin zone. In the case of non-coinciding extrema, a similar problem was investigated by Kozlov and Maksimov and by Cloizeaux[2]. It turned out that the energy of the electron-hole pairing decreases sharply if the symmetries of the electron and hole bands are different. For this reason, typical semimetals of the group V undergo no transition to the dielectric state when the temperature is lowered. In the case of a strong magnetic field, when the character of the electron and hole motion becomes one-dimensional and the Fermi surfaces contract to points,[3] electron-hole pairing turns out to be possible, as was indeed observed in Bi and Sb alloys in a magnetic field of ~ 35 kOe[4].

Owing to the electron phonon interaction, the phonon system in isotropic semimetals is also subject to instability[5]. When the extrema coincide, the instability sets in for phonons with zero momentum (appearance of soft modes). If the extrema do not coincide, the phonons that become unstable are those with a momentum $\hbar q_0$ characterizing the appearance of a new period in the system.

The Hamiltonian used in[1] did not include a term corresponding to interband transitions. In the present paper we investigate a model of the type considered in[1], but with allowance for interband transitions, in order to explain the electronic and structural transformations in compounds of the A_4B_6 type.

2. ELECTRON SPECTRUM AND STRUCTURE OF A_4B_6 SEMICONDUCTORS

Semiconductors of the A_4B_6 type are compounds of elements from groups IV and VI of the periodic system. The unit cell of the crystal lattice of such a compound contains one of each of the components A and B. Thus, there are 10 valence electrons per unit cell, just as in semimetals of group V. By now it can be regarded as established[6] that the extrema of the conduction band in the valence band of an A_4B_6 semiconductor (and its alloys), which has a lattice of the NaCl type, are located at L points of the Brillouin zone with symmetry group D_{3d}. Moreover, there exist numerous experimental facts evidencing that the symmetry of the electronic states in the extremal points in the empty and filled bands that are closest to each other are described by one-dimensional (without account of the spin) spinor representations L_6^+ and L_6^- of the group D_{3d}, and these states are genetically connected with single one-dimensional representations $L_1^+(A_1^+)$ and $L_2^-(A_1^-)$ of the same group[6].

Depending on the particular chemical composition of the compound, the state L_6^- can correspond either to the bottom of the conduction band or to the valence band. Thus, e.g., in PbTe the bottom of the conduction band belongs to the representation L_6^- and the top of the valence band to the representation L_6^+, whereas in the case of the cubic phase of SnTe the symmetry L_6^- corresponds to states at the top of the valence band, and the bottom of the conduction band has symmetry L_6^+ (it is assumed here and throughout that the unit cell and the Brillouin zone are centered about the cation—the atom of the group-IV).

In the series of $Pb_{1-x}Sn_xTe$ solid solutions, a gradual decrease of the width of the forbidden band is first observed, at $x \approx 0.35$, this width is equal to zero, and at $x > 0.35$ there appears again a dielectric gap, which now increases with increasing x. As a result, the alloy always remains a semiconductor. Dimock et al.[7] attribute this behavior of the width of the forbidden band to band inversion connected with relativistic effects. It is noted in the same paper that since the states L_6^+ and L_6^- are spin-degenerate, their crossing as a result of inversion does not cause a transition to the metallic state. It is precisely in systems with inverted band structure (such as SnTe) that conductivity anomalies are observed when the temperature is lowered[8], as well as a transition from the cubic to the rhombohedral phase[9]. The latter relates even closer the A_4B_6 compounds with the elements of group V, which crystallize just in the rhombohedral phase.

It will be shown below that a rearrangement of the crystal structure and of the electron spectrum should occur when the effective gap due to the Coulomb[1] or electron-phonon[5] interaction turns out to be of the order of or larger than the gap due to the interband transitions. The interband interaction then alters the character of the phase transition, making it a transition with a rigidly prescribed phase of the order parameter.

3. THE HAMILTONIAN

We divide the Hamiltonian $\hat{H}$ of the system investigated by us into three parts, $\hat{H}_0^e$, $\hat{H}_0^p$, and $\hat{H}_{int}$, where $\hat{H}_0^e$ is the Hamiltonian of the electrons that do not interact with one another and are in the periodic field of the lattice, $\hat{H}_0^p$ is the Hamiltonian of the free phonons, and $\hat{H}_{int}$ is the Hamiltonian describing the electron-electron and electron phonon interactions. Before we proceed to a concrete determination of the form of these operators, we make one simplifying assumption that does not affect qualitatively the results described below.

It was noted in the preceding section that the states of the conduction and valence bands near a point are classified in accord with spinor representations of the group D_{3d}. This calls for retention of the spinor index in all the calculations, which inevitably complicates the calculations. To avoid the use of the spinor indices, we shall henceforth assume that the spin-orbit interaction is negligibly small. Then in accordance with the premise advanced in Sec. 2, that the states of type L_6^+ and L_6^- stem predominantly from states corresponding to symmetries of one-dimensional single representations of the group D_{3d}, it must be assumed that the states of the bottom of the conduction band and of the top of the valence band belong in the inverted structure to the representations L_1^+ and L_2^-, respectively.

Now, leaving out the spin indices, we obtain the form of the Hamiltonian $\hat{H}_0^e$ in the representation of Luttinger and Kohn[10]. As will be shown subsequently, this representation is convenient in that, on the one hand, it has an explicitly separated interband-transition term that is bilinear in the electron creation and annihilation operators, and on the other hand the interaction Hamiltonian can be written in simplest form. The complete and orthonormal system of basis functions of this representation is

$$\psi_{n\mathbf{q}} = \psi_{n\mathbf{q}_0} e^{i\mathbf{q}\mathbf{r}} \equiv u_{n\mathbf{q}}(\mathbf{r}) \exp\{-i(\mathbf{q}-\mathbf{k}_0)\mathbf{r}\}, \tag{1}$$

where

$$\psi_{n\mathbf{k}_0} = u_{n\mathbf{k}_0}(\mathbf{r}) e^{i\mathbf{k}_0\mathbf{r}} \tag{2}$$

is the exact solution of the Schrödinger equation in a specified periodic potential of the lattice, known for a fixed value of the wave index k_0 in all the bands. Here n is the number of the band, and q is an arbitrary vector of the Brillouin zone, reckoned from the end of the vector k_0. Wave functions of the type (1) correspond to creation and annihilation operators $\overset{+}{a}_{nq}$ and a_{nq}. In the basis (1), the Schrodinger equation in a given periodic potential corresponds to the Hamiltonian

$$\sum_{\mathbf{q}n} \left\{ \frac{\hbar^2}{2m_0} \mathbf{q}^2 + \varepsilon_n(\mathbf{k}_0) \right\} \overset{+}{a}_{n\mathbf{q}} a_{n\mathbf{q}} + \sum_{\mathbf{q}nn'} \frac{\hbar}{m_0} \mathbf{P}_{nn'}\mathbf{q} \overset{+}{a}_{n'\mathbf{q}} a_{n\mathbf{q}}, \tag{3}$$

where m_0 is the mass of the free electron, $\epsilon_n(q_0)$ is the energy of a state with wave function (2), and the vector $P_{n'n}$ is defined by the equation

$$\mathbf{P}_{n'n} = -i\hbar \int d^3\mathbf{r} \psi_{n'\mathbf{k}_0}(\mathbf{r}) \nabla_{\mathbf{r}} \psi_{n\mathbf{k}_0}(\mathbf{r}). \tag{4}$$

Bearing in mind the concrete band structure of the semiconductors of the A_4B_6 group, it is convenient to choose as the vector k_0 a vector corresponding to the point L of the Brillouin zone. The symmetry of the states at this point is such that the diagonal matrix elements of the momentum operator (4) are equal to zero in it[11]. To describe the band structure of A_4B_6 semiconductors with inverted bands, we shall start with a model that takes into account the strong interaction (of the $P \cdot q$ type) of only two bands (conduction and valence), for in accord with the conclusions of Dimmock et al[7] it is the terms of just these bands that cross upon inversion. Then the influence of the remaining bands on the spectrum near the point L reduces only to a renormalization of the effective masses of the electrons in the states L_1^+ and L_2^-. We assume the renormalized mass m for both bands to be the same in absolute value and isotropic. The last assumption is not essential for the derivations that follow and is used only to simplify the formulas.

The mass-renormalization procedure is described in the book of Bir and Pikus[12] (Sec. 22) and makes it possible to obtain from (3) the Hamiltonian $\hat{H}_0^e$ which takes into account the interaction of the L_1^+ and L_2^- states and is the same for each prong of the star of the vector k_0:

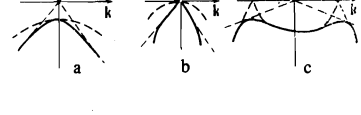
$$\hat{H}_0^e = \sum_{\mathbf{q}} \left[\varepsilon(\mathbf{q}) \overset{+}{a}_{1\mathbf{q}} a_{1\mathbf{q}} - \varepsilon(\mathbf{q}) \overset{+}{a}_{2\mathbf{q}} a_{2\mathbf{q}} + \frac{\hbar}{m_0} (\mathbf{P}\mathbf{q}) \overset{+}{a}_{1\mathbf{q}} a_{2\mathbf{q}} + \text{c.c.} \right]; \tag{5}$$

Here $\epsilon(q) = h^2q^2/2m - \epsilon_F$ and $\mathbf{P} = \mathbf{P}_{12}$ (see (4)). The energy is reckoned from the midpoint between the band extrema, and the subscripts 1 and 2 pertain to the states L_2^- and L_1^+, respectively.

We can now specify concretely the form of the matrix element of the interband interaction $(P \cdot q)$ in (5). Since the representations $L_2^-(A_1^-)$ and $L_1^+(A_1^+)$ are one-dimensional, and the symmetry D_{3d} contains an inversion, the factors $u_{nk_0}(r)$ in formula (2) for these representations can be chosen in the form of real functions. Then the vector $\mathbf{P} = \mathbf{P}_{12}$ (4) is pure imaginary. Further, according to the selection rules for the matrix elements of the polar vector between the states A_1^+ and A_1^-[11], only the z component of this vector differs from zero (the z axis is directed along k_0). Thus, the matrix element of the interband interaction can be written in our model in the form of Pqx, where x is the cosine of the angle between the vectors k_0 and q, while P and q are the lengths of the corresponding vectors, with the length of the vector P is pure imaginary.

The spectra of the Hamiltonian (5) are shown in the figure. The dashed line denotes the spectra without allowance for the interband transitions, and the solid line shows the point spectra. In case a the spectrum at the point L is represented prior to inversion ($\epsilon_F < 0$), in case b at the point of inversion ($\epsilon_F = 0$), and in case c the spectrum is far beyond the inversion point ($h|Pq_F|/m_0 < \epsilon_F$). Here q_F is the Fermi wave number.

Although it seems that in the real structures SnSe, SnTe, and GeTe the characteristic parameters of the interband, Coulomb, and electron-phonon interactions are of the order of unity, we consider the case of strong band overlap (case c in the figure), when there is a small parameter in the problem. One might assume that the qualitative conclusions of the theory remain unchanged also if a more realistic choice of this para-



meter is made. The relations between the different interaction constants are assumed arbitrary, and therefore all the interactions will be taken into account simultaneously. Since only the interband electron-electron and electron-phonon interactions give rise to a logarithmic singularity in the vertex part and in the polarization operator at P = 0[1,5], we express the interaction Hamiltonian in the basis (1) for each of the rays of the star of the vector k_0 in the form

$$\hat{H}_{int}=\sum_{\mathbf{p}_1,\mathbf{p}_2,\mathbf{q}}V(\mathbf{q})a^{+}_{1,\mathbf{p}_1-\mathbf{q}}a^{+}_{2,\mathbf{p}_2+\mathbf{q}}a_{2,\mathbf{p}_2}a_{1,\mathbf{p}_1} + \sum_{\mathbf{p},\mathbf{q}}\left[g(\mathbf{p},\mathbf{q})a_{1,\mathbf{p}}a_{2,\mathbf{p}+\mathbf{q}}(b_{\mathbf{q}}+b^{\cdot}_{-\mathbf{q}})+\text{c.c.}\right], \tag{6}$$

where b^{+}_{q} and b_q are the phonon creation and annihilation operators, V(q) is the screened Coulomb interaction, and g(p, q) is the electron-phonon coupling constant corresponding to the interband transitions. To simplify the notation we have retained in (6) the interaction with only one of the phonon modes, since these interactions differ from one another only in the form of the function g(p, q).

It must be noted that it is precisely the use of the Luttinger and Kohn basis which makes it possible to regard the matrix elements for the allowed transitions in (6) only as functions of the momentum transfer ħq for momenta smaller than the reciprocal lattice period. The reason is that in the basis (1) the Bloch factor $u_{nq}(\mathbf{r})$ does not depend on $q(u_{nq}(\mathbf{r}) \equiv u_{nq_0}(\mathbf{r}))$. We, however retain the dependence of the coupling constant g(p, q) on p because, first, we shall need later on to take into account transitions that are forbidden at the point L, and second, this dependence reflects the fact that, unlike the exact form (3), the two-band model (5) is valid only in the vicinity of the point L.

It is quite difficult to determine the form of the constants g(p, q) for the interaction between the electrons and an arbitrary phonon mode. However, inasmuch as the extrema of the electron and hole bands in our mode are at the same point L of the Brillouin zone, it suffices for us to know only the selection rules for the longitudinal optical and acoustic modes in the limit as q → 0. In this limit, the symmetry of the indicated modes is cubic (both modes are triply degenerate in the displacement directions), and therefore the symmetry and the selection rules for the electron-phonon interaction are determined only by the symmetry of the electronic states, which in turn is characterized by the directions of the vector P in the prong of the vector k_0. It is easy to verify that at the points L the transitions between states L_1^+ and L_2^+ with participation of optical phonons are allowed, and the corresponding coupling constant is proportional to the projection of the vector P on the direction of the sublattice displacement. Transitions in which extremely-long-wave acoustic phonons take part are strictly forbidden at the point L, since the states L_1^+ and L_2^- have different symmetries with respect to inversion. However, with increasing distance from the point L these transitions become allowed, and their amplitude is proportional to $q \cdot \delta P$ (where δP is the change of the vector P following acoustic deformation), as can be easily verified with the aid of expressions (4) and (5)).

We have thus determined the forms of the Hamiltonians $\hat{H}^e_0$, and $\hat{H}_{int}$. As to the phonon Hamiltonian $\hat{H}^p_0$, it has a standard form for each of the phonon modes:

$$\hat{H}_0{}^p=\sum_{\mathbf{q}}\hbar\omega(\mathbf{q})b_{\mathbf{q}}{}^{+}b_{\mathbf{q}}, \tag{7}$$

where ω(q) is the frequency of the corresponding phonon mode with wave number q.

4. SYSTEM OF FUNDAMENTAL EQUATIONS. EQUATIONS FOR THE ENERGY GAP

We consider a situation that arises when a system described by a Hamiltonian H is unstable against pairing of electrons and holes and against Bose condensation of optical phonons. We neglect for the time being interactions with acoustic phonons. We assume also that the indicated instability is connected with only one of the four prongs of the star of the vector k_0, i.e., we do not take into account the interaction of electrons located at different points L of the Brillouin zone via the phonon system. The latter is essential only for the determination of the true form of the lattice deformation, but does not affect the general properties of the phase transition.

To describe the stable state of the system in this case it is necessary to introduce, in addition to the normal Green's function for the electrons

$$G_{11}(\mathbf{p},t)=-i\langle Ta_2(\mathbf{p},t)a_1{}^{+}(\mathbf{p},0)\rangle \tag{8}$$

also the anomalous function

$$G_{21}(\mathbf{p},t)=-i\langle Ta_2(\mathbf{p},t)a_1{}^{+}(\mathbf{p},0)\rangle \tag{9}$$

and the nonzero anomalous mean value $\langle b_0 + b_0^{+}\rangle$ for the optical phonons which determines the sublattice displacement. The equation of motion for this average phonon field is

$$\left(-\frac{1}{\omega_0}\frac{\partial^2}{\partial t^2}-\omega_0\right)\langle b_0+b_0{}^{+}\rangle=4\,\mathrm{Im}\sum_{\mathbf{p}}g(\mathbf{p},0)G_{21}(\mathbf{p},+0), \tag{10}$$

where ω_0 is the energy of the optical phonons with zero momentum.

The equations for the electronic Green's functions (8) and (9) can also be readily obtained:

$$\begin{gathered}\left[i\frac{\partial}{\partial t}-\varepsilon(\mathbf{p})\right]G_{11}(\mathbf{p},t)-\left[\frac{\hbar}{m_0}\mathbf{P}^{*}\mathbf{p}+\Delta_e(\mathbf{p})\right.\\ \left.+g(\mathbf{p},0)\langle b_0+b_0{}^{+}\rangle\right]G_{21}(\mathbf{p},t)=\delta(t),\\ \left[i\frac{\partial}{\partial t}+\varepsilon(\mathbf{p})\right]G_{21}(\mathbf{p},t)-\left[\frac{\hbar}{m_0}\mathbf{P}\mathbf{p}+\Delta_e{}^{*}(\mathbf{p})\right.\\ \left.+g(\mathbf{p},0)\langle b_0+b_0{}^{+}\rangle\right]G_{11}(\mathbf{p},t)=0.\end{gathered} \tag{11}$$

With the aid of (10) we can find an expression for the average static lattice deformation in terms of G_{21} and substitute it in (11). In the energy representation, the system of equations for the electronic Green's functions takes the form

$$\begin{gathered}[\omega-\varepsilon(\mathbf{p})]G_{11}(\mathbf{p},\omega)-\left[\frac{\hbar}{m_0}\mathbf{P}^{*}\mathbf{p}+\Delta_e(\mathbf{p})+\Delta_\Phi(\mathbf{p})\right]G_{21}(\mathbf{p},\omega)=1,\\ [\omega+\varepsilon(\mathbf{p})]G_{21}(\mathbf{p},\omega)-\left[\frac{\hbar}{m_0}\mathbf{P}\mathbf{p}+\Delta_e{}^{*}(\mathbf{p})+\Delta_\Phi(\mathbf{p})\right]G_{11}(\mathbf{p},\omega)=0\end{gathered} \tag{12}$$

with the self-consistency conditions (g(p, 0) ≡ g(p))

$$\begin{gathered}\Delta_e(\mathbf{p})=\frac{i}{(2\pi)^4}\int d\omega\,d^3\mathbf{q}\,V(\mathbf{p}-\mathbf{q})G_{21}(\mathbf{q},\omega),\\ \Delta_{\mathrm{ph}}(\mathbf{p})=-\frac{4}{(2\pi)}g(\mathbf{p})\int d^3\mathbf{q}\,d\omega\,\mathrm{Im}\left[\frac{g(\mathbf{q})}{\omega_0}G_{21}(\mathbf{q},\omega)\right].\end{gathered} \tag{13}$$

By solving Eqs. (12) we determine the function G_{21}, which must be substituted in (13) to obtain a closed system of equations for the order parameters Δ_e and Δ_{ph}:

$$\Delta_e(\mathbf{p})=\frac{1}{2(2\pi)^3}\int d^3\mathbf{q}\,V(\mathbf{q}-\mathbf{p})\left[\frac{\hbar}{m_0}\mathbf{P}\cdot\mathbf{q}+\Delta_e(\mathbf{q})+\Delta_{ph}(\mathbf{q})\right]$$
$$\times\left[\varepsilon^2(\mathbf{q})+\left|\frac{\hbar}{m_0}\mathbf{P}\cdot\mathbf{q}+\Delta_e(\mathbf{q})+\Delta_{ph}(\mathbf{q})\right|^2\right]^{-1/2}$$
$$\Delta_{ph}(\mathbf{p})=\frac{2}{(2\pi)^3}g(\mathbf{p})\int d^3\mathbf{q}\frac{g(\mathbf{q})}{\omega_0}[\operatorname{Re}\Delta_e(\mathbf{q})+\Delta_{ph}(\mathbf{q})]$$
$$\times\left[\varepsilon^2(\mathbf{q})+\left|\frac{\hbar}{m_0}\mathbf{P}\cdot\mathbf{q}+\Delta_e(\mathbf{q})+\Delta_{ph}(\mathbf{q})\right|^2\right]^{-1/2}. \tag{14}$$

We have used here the fact that, inasmuch as the sublattice displacement $\langle b_0 + b_0^+\rangle$ is a real number, the electron-phonon coupling constant g(p) is also a real number under our choice of the phases of the electronic wave functions in (5).

It is impossible to obtain a solution of Eqs. (14) in general form. We therefore investigate first the limiting case of a short-range potential.

5. SOLUTION OF EQUATIONS FOR THE GAP IN THE CASE OF A SHORT-RANGE POTENTIAL

Assume that g(p) in (14) is equal to zero, and that the potential V(q − p) can be replaced by an effective momentum-independent coupling constant λ, which vanishes, however, at momentum transfers $\hbar q > \hbar q_F$, where $\hbar q_F$ is the Fermi momentum. The last condition ensures convergence of the integral in (14). We can now integrate in (14) with respect to the angle variables, and the result of the integration depends on whether we are calculating the real or imaginary part of the electron gap, $\Delta' = \operatorname{Re}\Delta_e$ or $\Delta'' = \operatorname{Im}\Delta_e$. We have

$$\Delta'=\frac{\lambda\Delta'}{2(2\pi)^2}\int_0^q dq\frac{m_0 q}{\hbar|P|}\ln\frac{A}{B}, \tag{15}$$

$$\Delta''=\frac{\lambda}{2(2\pi)^2}\int_0^{q_F} dq\frac{m_0 q}{\hbar|P|}\left(A-B+\left|\frac{\hbar}{m_0}|P|q-\Delta''\right|-\left|\frac{\hbar}{m_0}|P|q+\Delta''\right|\right); \tag{16}$$

here

$$A=\left|\frac{\hbar}{m_0}|P|q+\Delta''\right|+\left[\left(\frac{\hbar}{m_0}|P|q+\Delta''\right)^2+\Delta'^2+\varepsilon^2(q)\right]^{1/2},$$
$$B=\left|\frac{\hbar}{m_0}|P|q-\Delta''\right|+\left[\left(\frac{\hbar}{m_0}|P|q-\Delta''\right)^2+\Delta'^2+\varepsilon^2(q)\right]^{1/2}.$$

Both (15) and (16) admit of the trivial solution $\Delta_e = 0$. Nontrivial solutions can be obtained only approximately, with logarithmic accuracy. To this end, separating the singularity near the Fermi energy ϵ_F, we obtain in the usual manner from (15) and (16), respectively,

$$\frac{1}{\tilde\lambda}=\ln\frac{16\varepsilon_F^2}{CD}+2, \tag{17}$$
$$\frac{1}{\tilde\lambda}=\ln\frac{16\varepsilon_F^2}{CD}-1, \tag{18}$$

where

$$C=\left[\left(\frac{\hbar}{m_0}|P|q_F+\Delta''\right)^2+\Delta'^2\right]^{1/2},$$
$$D=\left[\left(\frac{\hbar}{m_0}|P|q_F-\Delta''\right)^2+\Delta'^2\right]^{1/2}$$

and the effective coupling constant $\bar\lambda$ is equal to

$$\tilde\lambda=\lambda q_F^3/4(2\pi)^2\varepsilon_F. \tag{19}$$

The general solution of the system of (17) and (18) for the parameter Δ_e can be represented in the form

$$\Delta_e=\left(\Delta_0'^2-\left(\frac{\hbar}{m_0}|P|q_F\right)^2\right)^{1/2}\ \text{at}\ \operatorname{Im}\Delta_e=0, \tag{20a}$$

$$\Delta_e=i\left(\Delta_0''-\frac{\hbar}{m_0}|P|q_F\right)\ \text{at}\ \operatorname{Re}\Delta_e=0,\quad |\Delta_0''|>\frac{\hbar}{m_0}|P|q_F, \tag{20b}$$

where

$$\Delta_0'=4\varepsilon_F\exp\{-1/2\tilde\lambda+1\},\qquad \Delta_0''=4\varepsilon_F\exp\{-1/2\tilde\lambda-1/2\}. \tag{21}$$

Thus, Eq. (14) admits of solutions for the gap with arbitrary phase, but it follows from (20) and (21) that at a given coupling constant the largest gap corresponds to zero phase. In other words, the maximal gap is produced when its phase differs from the phase of the amplitude of the interband transition by π/2. Calculating the ground-state energy correction necessitated by the appearance of the gap, it is easy to find that it is proportional to the square of the modulus of the gap, with minus sign. Consequently, the maximum modulus of the gap at a given coupling constant corresponds also to the minimum energy. Thus, the solution for the order parameter Δ_e turns out to be invariant to a gauge transformation of the first kind (the ground state is not degenerate in phase).

The phase of the solution is determined, accurate to π, by the phase of the interband-transition term (4). This leads to violation of the conditions for the validity of the Goldstone theorem concerning the existence of a spectrum of collective excitations filling the entire gap Δ_e, and consequently our system does not have the superfluidity properties connected with the presence of the gap Δ_e. Indeed, any collective motion with momentum $\hbar p$ is connected with the appearance in the expression for the order parameter of a phase factor of the type e(ip · r). We have seen, however, that the energy of the ground state depends on the phase and consequently, even in the limit of long waves (p → 0) the "elasticity" of the system remains finite, thus ensuring a finite frequency (energy) to the collective motions in the long-wave limit.

Thus, the most convenient solution for the electron gap, from the thermodynamic point of view, is given by

$$\Delta_e=\pm\operatorname{Re}\left[\Delta_0'^2-\left(\frac{\hbar}{m_0}|P|q_F\right)^2\right]^{1/2}, \tag{22}$$

and the correction δE to the ground-state energy is then

$$\delta E\backsim\left[\left(\frac{\hbar}{m_0}|P|q_F\right)^2-\Delta_0'^2\right]\theta\left(\Delta_0'^2-\left(\frac{\hbar}{m_0}|P|q_F\right)^2\right), \tag{23}$$

where

$$\theta(x)=\begin{cases}1 & \text{if}\ x>0\\ 0 & \text{if}\ x<0\end{cases}.$$

It is seen from (23) that at the instant when the phase transition takes place, the correction to the energy of the ground state is small, but is determined by the difference of two finite quantities, each of which depends on the parameters of the real crystal. This in turn causes the first derivatives of this quantity (and of the pressure) with respect to the crystal parameters (say the volume) to be finite, in spite of the smallness of δE (and consequently the smallness of the pressure in the system). Therefore the crystal is unstable to finite changes of its parameters, once a nontrivial solution of Δ_e is obtained. The system therefore becomes restructured jumpwise in such a way that it again becomes stable. A first-order phase transition takes place. In our problem, the described situation arises as a result of the presence in the initial Hamiltonian of a term causing interband transitions.

It can thus be concluded that the interband transitions described by the expression $\hbar\mathbf{P}\cdot\mathbf{q}a_1^+a_2/m_0$ (5) lead directly to two effects in the presence of instability in the system relative to electron-hole pairing. With increasing interband-interaction term, the second-order phase transition becomes a first-order transition and the lower-symmetry system restructured as a result of the phase transition has no collective-excitation branches with zero frequency in the long-range limit.

In concluding this section it must be noted that the possibility, considered by Guseĭnov and Keldysh[15], of a first-order phase transition resulting from an interaction of the type $\tilde{V}a_1^+a_1^+a_2a_2$ is analogous to that indicated above, since the interband transitions contained in the Hamiltonian (5) generate similar terms from expression (7).

6. SELF-CONSISTENT SOLUTION FOR A FIRST-ORDER PHASE TRANSITION

We now obtain a self-consistent solution for a first-order phase transition, taking into account the interaction of the electrons with one another as well as their interaction with optical and acoustic phonons. As shown by an investigation carried out in the preceding section, the electron-hole interaction gives rise to the appearance of a dielectric gap, the phase shift of which in the ground state coincides with the phase of the phonon gap Δ_{ph}. This follows directly from expressions (22) and (14). Therefore a simultaneous allowance for the electron-hole interaction and of the interaction of the electrons with the optical phonons causes no difficulties and leads simply to an effective increase of the electron-phonon coupling in the equation for the phonon gap Δ_{ph} (see formula (14)) as a result of the electron-hole interaction. The solution of this equation coincides exactly with the solution of the equation for the real part of the electron gap (22), (21), which was obtained in Sec. 5, and differs from it only in the value of the coupling constant.

It is also shown in Sec. 5 that in fact a solution of the type (22) is unstable near the phase-transition point because at this point it is not extremal with respect to all degrees of freedom of the crystal. Let us assume (although this assumption is not necessarily fulfilled), that the main parameter, with respect to which the requirement that the energy be extremal at the phase-transition point be extremal is violated, is the interband-interaction parameter (4) itself. As shown in Sec. 3, the change of this parameter can be due to longitudinal deformation of the crystal and can be described in terms of the interaction of the electrons with the acoustic phonons. The problem of the phase transition then reduces to a joint solution of a system of equations of the type (14), the only difference being that instead of an equation for the electronic part of the gap we have an equation for the gap that occurs following longitudinal deformation ϵ, describing the interaction of the electrons with the acoustic phonons, the wave vector of which tends to zero, and the equation for Δ_{ph} contains a new coupling constant. The self-consistency equation for ϵ is given by

$$\varepsilon=\frac{2\alpha P^{*}}{c^2\rho(2\pi)^3|P|}\int d^3\mathbf{q}\frac{\hbar}{m_0}\mathbf{Pq}(\alpha\varepsilon-1)\left[\varepsilon^2(\mathbf{q})+\left|\frac{\hbar}{m_0}\mathbf{Pq}(1-\alpha\varepsilon)\right|^2+\Delta_{\text{ph}}^2\right]^{-1/2},\tag{24}$$

where c is the velocity of the longitudinal sound in the crystal and ρ is the density of the material. Equation (24), unlike Eq. (14) for the gap Δ_{ph}, was written with the relative deformation used as the quasimean value of the field of the acoustic phonons, since this deformation is finite on both sides of the phase-transition point. In addition, it is assumed that the deformation takes place along the principal symmetry axis of one of the nonequivalent points L. This allows us to confine ourselves to only one component of the strain tensor ϵ_{ij} when writing down the matrix element of the electron-phonon interaction in the form $\alpha\epsilon_{ij}P_jq_i$. One can expect to obtain $\alpha\sim 1$ from dimensionality considerations.

Integrating in (24), we obtain

$$\begin{gathered}\varepsilon=\frac{1}{2}\gamma(\varepsilon-1)\ln\left\{16\varepsilon_F^2\left(\left|\frac{\hbar}{m_0}Pq_F(1-\varepsilon)\right|^2+\Delta_{\text{ph}}^2\right)^{-1}\right\},\\ \gamma=\frac{1}{3\pi^2}\cdot\frac{1}{cp^2}\left|\frac{\hbar}{m_0}Pq_F\right|^2\frac{q_F^3}{\varepsilon_F},\end{gathered}\tag{25}$$

where γ is the effective constant of the coupling with the acoustic deformation. In (25) and in the following we assume $\alpha = 1$.

Equation (25) must be solved simultaneously with the equation for the dielectric gap Δ_{ph} connected with the interaction of the electrons with one another and with the optical phonons. This equation is obtained by a simple generalization of (15). It is of the form

$$\Delta_{\text{ph}}\frac{1}{\lambda}=\Delta_{\text{ph}}\frac{1}{2}\ln\left\{16\varepsilon_F^2\left(\left|\frac{\hbar}{m_0}Pq_F(1-\varepsilon)\right|^2+\Delta_{\text{ph}}^2\right)^{-1}\right\},\tag{26}$$

where in accord with the foregoing the constant λ takes into account the interaction of the electrons with the optical phonons and with one another.

We can now note the following. Let the system (25) and (20) admit of a nontrivial solution for Δ_{ph} (there exists no trivial solution for ϵ). Then at $\Delta_{\text{ph}}\neq 0$ and $\lambda<\gamma$ the longitudinal deformation $\epsilon=\epsilon_1$ is given by

$$\varepsilon_1=\gamma/(\gamma-\lambda),\tag{27}$$

and at $\Delta_{\text{ph}}\equiv 0$ we get a value $\epsilon=\epsilon_0<0$ that does not depend on λ (25). From (27) it follows that $\epsilon_1>0$ (at $\gamma>\lambda$) and increases with increasing λ, thus evidencing that the crystal expands along the chosen prong of the vector $\mathbf{k}_0$.

From the requirement $\Delta_{\text{ph}}^2\geq 0$ follows a condition for the existence of a nontrivial solution (of its point of absolute instability):

$$4\varepsilon_Fe^{-1/\lambda}\geqslant|\hbar Pq_F/m_0|(1-\varepsilon_1),\tag{28}$$

and a condition for the appearance of a nontrivial solution (a point of absolute instability of the trivial solution):

$$4\varepsilon_Fe^{-1/\lambda}\geqslant|\hbar Pq_F/m_0|(1-\varepsilon_0).\tag{29}$$

It is obvious that in the general case the limiting values of the coupling constants, determined from the inequalities (28) and (29), do not coincide, and this is also evidence of a first-order phase transition.

To assess which of the solutions, the trivial one (ϵ_0, $\Delta_{\text{ph}}=0$) or the nontrivial one (ϵ_1, $\Delta_{\text{ph}}\neq 0$), is thermodynamically more favored near this value of the coupling constant at which the trivial solution appears, it is necessary to determine which of the solutions corresponds to the absolute minimum of the energies. From an analysis of the preceding section (and on the basis of the result obtained in this section for not too large values of λ) we can state, however, that solutions with small order parameters Δ_{ph} are unstable, and this leads to first-order phase transitions, and consequently to a finite frequency of the "soft" optical mode at the transition point. This is easiest to verify by calculating the corresponding polarization operator

$$\pi(\mathbf{k},\omega) = -ig^2(\mathbf{k})\sum_{\mathbf{p}}\left\{\int\frac{d\omega_1}{2\pi}G_{11}(\mathbf{p}+\mathbf{k},\omega_1+\omega)G_{22}(\mathbf{p},\omega_1) + \int\frac{d\omega_1}{2\pi}G_{21}(\mathbf{p}+\mathbf{k},\omega_1+\omega)G_{21}(\mathbf{p},\omega_1)\right\}. \tag{30}$$

We see that at a finite value of Δ_{ph} we have at the phase-transition point $\omega(q = 0) \neq 0$. In final analysis, the reason why Δ_{ph} is finite is that the interband term $hP \cdot qa_1^+a_2/m_0$ is finite.

7. DISCUSSION OF RESULTS

It was shown in the preceding sections that, owing to the instability of the electron-phonon system relative to pairing of the electrons and holes from different bands and owing to Bose condensation of the optical phonons, a first-order phase transition is produced and becomes closer to a second-order transition to a degree that depends on the interband interaction of the type $\hbar P \cdot qa_1^+a_2/m_0$. The transition is accompanied by a deformation (dilatation) of the lattice along the direction singled out by the vector P. These results were obtained for a one-ellipsoid model. In real A_4B_6 structures there are four equivalent directions. One can expect, however, that since these directions cannot be mutually orthogonal, and the coupling constant with the optical phonons is maximal, from symmetry considerations (Sec. 3), for sublattice displacements in the directions of equivalent axes, the phase transition will occur only in one group of electronic extrema. The point is that, owing to the nonorthogonality of the axes, the deformation and the sublattice shift affect the electronic states that oriented along the three other axes, and the sublattice shift is energywise most favored in one of the directions of the vector k_0 of the star, because the size of the gap depends exponentially on the constant for the coupling with the optical phonons, a coupling that is anisotropic with respect to the polarization of the oscillations. Owing to the presence of a rhombohedral distortion, the points L and T of the Brillouin zone become nonequivalent, and the shift of the extrema, due to this distortion, is different for different bands. It may turn out that the maximum of the valence band at the point T will lie lower than the minimum of the conduction band at the point L, i.e., a semimetal is produced. There are indications that the spectrum has a semimetallic character in the rhombohedral phase of SnTe[16].

Timerov and one of us[17] have shown, for a model with interband transitions similar to the one considered here, that the electron-hole pairing at unequal electron and hole densities can lead to an increase in the superconducting transition temperature. It is known that it is precisely in A_4B_6 semiconductors with inverted bands that superconductivity appears after doping. In accordance with the considered model, a correlation between the temperatures of the superconducting and structural transitions has been experimentally established[16]. Thus, these semiconductors behave, from the point of view of superconductivity, like compounds of transition metals with β-W structure, in which there is a low-temperature tetragonal restructuring of the lattice, as against the rhombohedral one in the A_4B_6 semiconductors.

The reasons for the rather high superconducting transition temperatures in A_4B_6 compounds may be, besides the usually considered softening of the optical phonon mode, also the restructuring of the electronic spectrum[13,17] and the smallness of the interband Coulomb interaction of the electrons at large ($\sim \hbar q_F$) momentum transfers. The latter is due to the strong non-orthomality of the factors $u_k(r)$ at different k in the exact Bloch wave functions, owing to the interband transition term $\hbar P \cdot qa_1^+a_2/m_0$, which alters strongly the eigenfunctions of the Hamiltonian $\hat{H}_0^e$.

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[1] L. V. Keldysh and Yu. V. Kopaev, Fiz. Tverd. Tela **6**, 2791 (1964) [Sov. Phys.-Solid State **6**, 2219 (1965)].

[2] A. N. Kozlov and L. A. Maksimov, Zh. Eksp. Teor. Fiz. 48, 1184 (1965) [Sov. Phys.-JETP **21**, 790 (1965)]. J. Cloizeaux, J. Phys. Chem. Sol. **26**, 259 (1965).

[3] A. A. Abrikosov, J. Low Temp. Phys. **2**, 37, 175 (1970).

[4] N. B. Brandt and S. M. Chudinov, ZheTF Pis. Red. **13**, 146 (1971) [JETP Lett. **13**, 102 (1971)].

[5] Yu. V. Kopaev, Fiz. Tverd. Tela 8, 2633 (1966) [Sov. Phys.-Solid State 8, 2106 (1967)].

[6] I. M. Tsidil'kovskiĭ, Élektrony i dyrki v poluprovodnikakh (Electrons and Holes in Semiconductors), Nauka, 1972.

[7] J. O. Dimmok, I. Melngailis, A. J. Stauss, Phys. Rev. Lett. **16**, 1193 (1966).

[8] G. F. Hoff, J. R. Dixon, Sol. St. Comm. **10**, 433 (1972).

[9] S. I. Novikov, L. E. Shelimova, Fiz. Tverd. Tela **7**, 2544 (1965); **9**, 1336 (1967) [Sov. Phys.-Solid State **7**, 2052 (1966), **9**, 1046 (1967)]. P. P. Seregin and E. P. Savin, ibid. **13**, 2790 (1971) [**13**, 2336 (1972)]. R. T. Bate, D. L. Carter, J. S. Wrobel, Phys. Rev. Lett. **25**, 159 (1970). L. Muldawer, Bull. Am. Phys. Soc. **16**, 84 (1971).

[10] W. Kohn, J. M. Luttinger, Phys. Rev. **97**, 869 (1955).

[11] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz, 1963 [Pergamon, 1965].

[12] G. L. Bir and G. E. Pikus, Simmetriya i deformatsionnye éffekty v polurpovodnikakh (Symmetry and Deformation Effects in Semiconductors), Nauka, 1972.

[13] Yu. V. Kopaev and R. Kh. Timerov, Zh. Eksp. Teor. Fiz. 63, 290 (1972) [Sov. Phys.-JETP **36**, 153 (1973)].

[14] J. Goldstone, Nuovo Cim. **19**, 154 (1961).

[15] R. R. Guseĭnov and L. V. Keldysh, Kratkie soobshcheniya po fizike (FIAN), No. 7, 58 (1971).

[16] D. H. Damon, C. R. Martin, and R. C. Miller, J. Appl. Phys. 34, 3083 (1963).

[17] Yu. V. Kopaev and R. Kh. Timerov, Fiz. Tverd. Tela 14, 86 (1972) [Sov. Phys.-Solid State 14, 69 (1972)].

[18] A. D. C. Grassie, A. Benyon, Phys. Rev. Lett. **39A**, 199 (1972).

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